

*Reprinted from*

# Applied Physics Letters

Volume 65

26 September 1994

Number 13

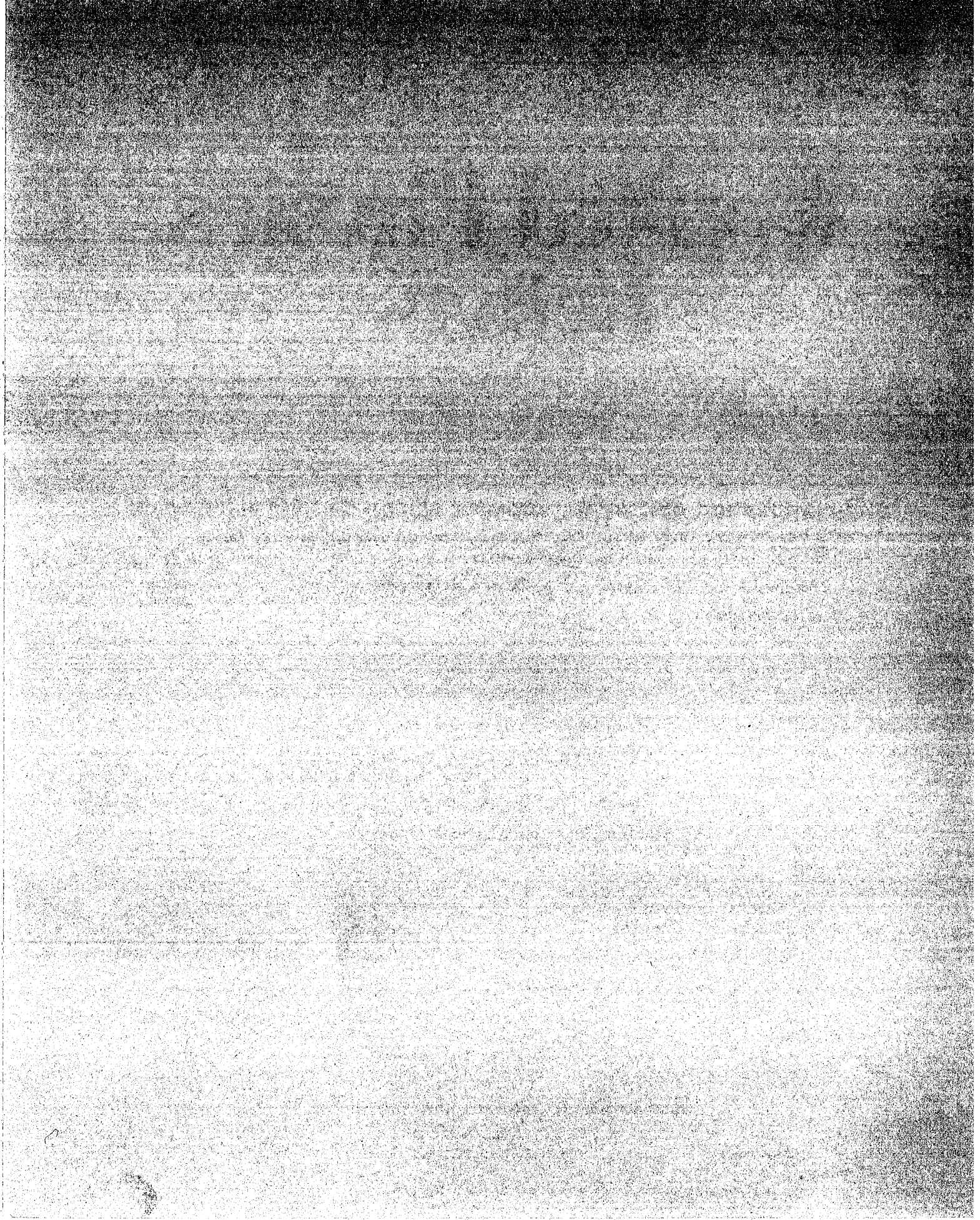
## **Site-competition epitaxy for superior silicon carbide electronics**

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(Received 4 May 1994; accepted for publication 26 July 1994)

pp. 1659-1661

a publication of the American Institute of Physics





# Site-competition epitaxy for superior silicon carbide electronics

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We present and discuss a novel dopant control technique for compound semiconductors, called site-competition epitaxy, which enables a much wider range of reproducible doping control and affords much higher and lower epilayer doping concentrations than was previously possible. Site-competition epitaxy is presented for the chemical vapor deposition of 6H-SiC epilayers on commercially available (0001)SiC silicon-face substrates. Results from utilizing site-competition epitaxy include the production of degenerately doped SiC epilayers for ohmic-as-deposited (i.e., unannealed) metal contacts as well as very low doped epilayers for electronic devices exhibiting SiC record-breaking reverse voltages of 300 and 2000 V for 3C- and 6H-SiC *p-n* junction diodes, respectively.

Silicon carbide (SiC) is emerging as a material of choice for fabrication of high power and/or microwave-frequency semiconductor devices suitable for operation in high temperature, high radiation, and corrosive environments. However, in order for the inherently superior high-temperature semiconductor properties of SiC to be realized in advanced electronic device applications, control over the electronic properties of chemical vapor deposited (CVD) epitaxial layers must be improved. Prior to this work, control over dopant incorporation for CVD SiC epilayers had been limited, with reproducible doping typically confined to doping concentrations ranging from  $N_D \approx 2 \times 10^{16} \text{ cm}^{-3}$  to  $5 \times 10^{18} \text{ cm}^{-3}$  for *n* type and from  $N_A \approx 2 \times 10^{16} \text{ cm}^{-3}$  to  $1 \times 10^{18} \text{ cm}^{-3}$  for *p*-type 6H-SiC epilayers.<sup>1,2</sup> Expanding the reproducible doping range to include lower concentrations would enable the fabrication of multikilovolt SiC power devices, whereas the availability of higher doping concentrations would result in devices with increased performance because of lower parasitic resistances.

In this letter we report on an epilayer growth process, called site-competition epitaxy, which serves to increase the reproducibility of CVD epilayers while greatly expanding the doping range for both *n*-type and *p*-type CVD SiC epilayers.<sup>3</sup> Previously, we reported our preliminary findings that the silicon-to-carbon (Si/C) ratio within the growth reactor strongly affects dopant incorporation for epilayers grown on the (0001)6H-SiC silicon face (Si-face). We named this process site-competition epitaxy.<sup>4</sup> Similar results were obtained during subsequent experiments using this technique for SiC epitaxy on SiC(1210) *a*-face substrates<sup>5</sup> and also on our 3C-SiC(111) and 4H-SiC(0001) Si-face basal plane substrates. Preliminary results indicate that site-competition epitaxy is not applicable for epilayers grown on (0001) 6H-SiC carbon-face substrates.

Here, we present experimental results which demonstrate site-competition epitaxy using nitrogen and aluminum as dopant sources for CVD SiC epilayers grown on 6H-SiC(0001) off-axis Si-face substrates. The SiC epilayers were grown at 1450 °C on commercially available<sup>2</sup> *n*-type Si-face SiC substrates polished 3° off-axis from the (0001) plane towards the (1210) plane. The SiC substrates were placed onto a SiC-coated graphite susceptor and loaded into

a water-cooled quartz reactor of an atmospheric pressure CVD system.<sup>6</sup> The SiC epilayers were grown using silane (3% in H<sub>2</sub>) and propane (3% in H<sub>2</sub>) with a hydrogen carrier gas, resulting in  $\sim 3 \text{ } \mu\text{m/h}$  growth rates, and doped using either nitrogen (for *n*-type) or trimethylaluminum (TMA) (for *p*-type). The epilayers were characterized using secondary ion mass spectrometry (SIMS) analysis, mercury-probe or *p-n* diode capacitance voltage (*C-V*), low-temperature photoluminescence spectroscopy (LTPL), and Hall mobility measurements.

Site-competition epitaxy is a dopant control technique based on appropriately adjusting the Si/C ratio within the growth reactor to effectively control the amount of dopant incorporated into substitutional SiC crystal lattice sites. These sites are either carbon lattice sites (C sites) or silicon lattice sites (Si sites) located on the active growth surface of the silicon carbide crystal. Our model for site-competition epitaxy is based on the principle of competition between nitrogen and carbon for the C sites and between aluminum and silicon for the Si sites of the growing silicon carbide epilayer. The concentration of *n*-type (nitrogen) dopant atoms incorporated into a growing silicon carbide epilayer is decreased by increasing the carbon-source concentration so that C outcompetes N for the C sites. Analogously, the amount of *p*-type dopant (aluminum) incorporated is decreased by increasing the silicon-source concentration within the growth reactor so that Si outcompetes Al for the Si sites. This model is consistent with the previous work of Choyke<sup>7</sup> and Davis *et al.*,<sup>8</sup> in which they concluded from spectroscopic evidence that nitrogen atoms occupy C sites whereas aluminum atoms occupy Si sites of the SiC lattice.

In order to test the site-competition model we performed a series of *p*-type and *n*-type doping experiments in which only the propane concentration was varied to effectively change the Si/C ratio, while maintaining a constant silane and dopant-source concentration. These experiments were designed to determine the effect of varying the Si/C ratio on aluminum and nitrogen dopant incorporation into CVD SiC epilayers. For the *p*-type doping experiments, the propane concentration was the only parameter varied (400–2000 at. ppm) to effectively change the Si/C ratio within the growth reactor while the silane (200 at. ppm) and TMA (2

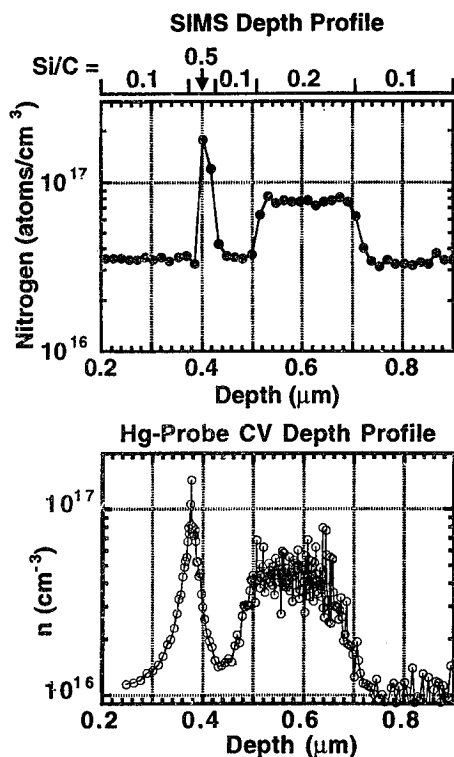


FIG. 1. A direct comparison between a SIMS profile analysis (top) and a mercury-probe  $C$ - $V$  electrical result for a sample grown by varying only the carbon-source concentration (400–1800 at. ppm) while maintaining a constant silicon-source concentration (200 at. ppm) and a constant nitrogen concentration (180 at. ppm) within the CVD reactor during SiC epilayer growth.

sccm  $H_2$  flow through a constant room-temperature TMA bubbler) flows were held constant. The purpose of the  $p$ -type doping experiments was to determine if a relative increase in silicon concentration (from an increase in the Si/C ratio) could be used to exclude aluminum from a growing SiC epilayer. Experiments performed using a Si/C ratio of 0.1 yielded degenerately doped  $p$ -type epilayers with net carrier concentrations of  $p \geq 1 \times 10^{19} \text{ cm}^{-3}$ . An otherwise identical set of  $p$ -type doping experiments were performed, except using a Si/C ratio of 0.5, which resulted in  $p$ -type epilayers with net carrier concentrations of  $p \approx 5 \times 10^{16} \text{ cm}^{-3}$ . These experimental results support the hypothesis that as the Si/C ratio is increased from 0.1 to 0.5, the relative amount of Si increases and outcompetes the Al for available Si sites of the growing SiC lattice, which ultimately results in decreased Al dopant incorporation.

During the growth of  $n$ -type doped epilayers, the silane (200 ppm) and molecular nitrogen (90 ppm) concentrations were held constant while the propane concentration was varied between 133 and 600 ppm. The nitrogen dopant profiles were characterized using SIMS and mercury-probe  $C$ - $V$ . The results for one such experiment are shown in Fig. 1. The SIMS profile (Fig. 1 top) exhibits variations of atomic nitrogen concentration within the grown epilayer from varying only the Si/C ratio (between 0.5 and 0.1) during epilayer growth. The net carrier concentration profile obtained from mercury-probe  $C$ - $V$  for the same sample (bottom of Fig. 1) correlates well with the SIMS profile. These results indicate

that site-competition epitaxy can be used to control dopant incorporation into electrically active crystal sites of the growing SiC epilayer.

To verify the reproducibility of site-competition epitaxy, a number of growth experiments were performed using the Si/C ratio extremes (0.1 and 0.5) while maintaining constant Si (200 at. ppm) and N (100 at. ppm) concentrations. Numerous 2-h growth experiments, using only the Si/C=0.1 ratio, consistently resulted in intentionally doped  $n$ -type epilayers with net carrier concentrations of  $n \approx 3 \times 10^{15} \text{ cm}^{-3}$ . In contrast, another set of 2-h epilayer growth experiments, using a Si/C=0.5 ratio, consistently resulted in  $n$ -type epilayers with  $n \approx 3 \times 10^{17} \text{ cm}^{-3}$ . According to our model, the decreased concentration of carbon relative to silicon (from increasing the Si/C ratio from 0.1 to 0.5) allows the nitrogen to outcompete the carbon for C sites of the growing SiC lattice, resulting in an increased atomic nitrogen incorporation.

Very low-doped epilayers were produced by using site-competition epitaxy to exclude the unintentional dopant atoms contained in the growth reactor from incorporating into the grown SiC epilayers. These unintentionally doped epilayers, grown using a Si/C=0.1, were examined using LTPL spectroscopy to determine the crystalline perfection and relative concentration of dopant incorporated during growth. The LTPL results from our lowest unintentionally doped  $p$ -type epilayer resulted in an  $I_{77}/P_0 = 150$  and  $I_{77}/S_0 = 4.7$ , indicating the most intrinsic SiC reported to date.<sup>9</sup> This is based on previous reports that the dopant concentration in SiC is correlated with the  $I_{77}/P_0$  and  $I_{77}/S_0$  peak-height ratios for low-doped SiC, where  $P_0$  and  $S_0$  are the nitrogen donor no phonon line intensities at 3.00 eV and at 2.99 eV, respectively, and  $I_{77}$  is the peak intensity of the SiC 77-meV intrinsic phonon replica at 2.947 eV.<sup>10,11</sup> This previous work indicates that the  $I_{77}/P_0$  intensity ratio increases as both the crystalline perfection increases and as the dopant concentration decreases in the SiC epilayer. Using these ratios, a  $1 \times 10^{14} \text{ cm}^{-3}$  estimate of unintentional dopant concentration was made by LTPL, which is consistent with our mercury-probe  $C$ - $V$  room-temperature measurements of  $p < 5 \times 10^{14} \text{ cm}^{-3}$ .

As discussed above, site-competition epitaxy can be used as a dopant-exclusion growth technique for the production of very low-doped SiC epilayers. Analogously, degenerately doped epilayers are produced by applying site-competition epitaxy to promote enhanced inclusion of dopant atoms during SiC epilayer growth. Very thin degenerately doped  $p$ -type and  $n$ -type contact layers are formed by ceasing the source flow of Si or C, respectively, during the final 30–40 s of epilayer growth and during substrate cooling. This allows the dopant atoms to incorporate into the topmost growing  $p$ -type or  $n$ -type epilayer without competition from the Si or C atoms, respectively. For example, degenerate  $n$ -type epilayers are produced by ceasing only the propane flow during the remaining 30–40 s of epilayer growth, while both the silane (200 at. ppm) and nitrogen (300 at. ppm) flows are maintained.

The metal contacts deposited on both the  $p$ -type and  $n$ -type degenerate epilayers are “ohmic-as-deposited” (i.e., unannealed) for a number of metals, which include alumi-

num, titanium, nickel, and molybdenum. Contact resistivities determined for as-deposited molybdenum and titanium were calculated [linear transmission line method (TLM)] to be  $p_c < 5 \times 10^{-5} \Omega \text{ cm}^2$  and  $p_c < 2 \times 10^{-5} \Omega \text{ cm}^2$ , respectively, on both *n*-type and *p*-type degenerately doped epilayers.<sup>12,13</sup>

The ohmic-as-deposited state of the contacts on the degenerately doped epilayers precluded conventional *C-V* profiling for the determination of net carrier concentrations. However, preliminary Hall measurements have been accomplished on intentionally doped *n*-type 6H-SiC epilayer samples. At room temperature, the degenerately doped *n*-type contact epilayers had measured low-electric-field free-carrier concentrations of  $n = 4 \times 10^{18} \text{ cm}^{-3}$  and yielded mobilities near  $60 \text{ cm}^2 \text{ V s}$ . When incomplete ionization is taken into account, the  $n = 4 \times 10^{18} \text{ cm}^{-3}$  low-field free-carrier concentration theoretically translates into atomic nitrogen concentrations in excess of  $N_D = 2 \times 10^{19} \text{ cm}^{-3}$ .<sup>14</sup> The higher electric fields exerted by the *C-V* technique (relative to the Hall technique) lead to higher measured free-carrier concentrations because of field-enhanced ionization that takes place within the high-field depletion region of a Schottky diode.<sup>15</sup> Relatively lighter-doped *n*-type epilayers with  $n = 8 \times 10^{16} \text{ cm}^{-3}$  had room-temperature Hall mobilities ranging from 247 to  $253 \text{ cm}^2 \text{ V s}$  and were found to be less than 10% compensated.

Superior SiC electronic devices have been produced in our laboratory by utilizing site-competition epitaxy. These devices exhibited superior electrical performance because the increased doping range resulting from utilizing site-competition epitaxy allows fabrication of SiC devices with much higher blocking voltages and lower parasitic resistances. Included among the device accomplishments are high voltage 6H-SiC diodes (2000 V) and 3C-SiC diodes (300 V) which exhibit the largest 6H- and 3C-SiC blocking voltages reported to date.<sup>16,17</sup>

In summary, a novel growth method, based on the use of appropriate Si/C ratios during epilayer growth to affect control over dopant incorporation, has been demonstrated for (0001) Si-face 6H-, 4H-SiC and (111) Si-face 3C-SiC. We have proposed a model, called site-competition epitaxy, which is based on competition between nitrogen and carbon for the C sites and between aluminum and silicon for the Si sites of the growing silicon carbide crystal. The nitrogen donor concentration in the grown epilayer is proportional to the Si/C ratio during epilayer growth, whereas the aluminum ac-

ceptor concentration is inversely proportional to the Si/C ratio. This growth technique was used to produce very low-doped epilayers for 6H-SiC and 3C-SiC diodes which exhibit SiC record blocking voltages of 2000 and 300 V, respectively. The technique was also used to grow degenerately doped epilayers which result in ohmic-as-deposited (i.e., unannealed) contacts for a variety of metals on both *p*-type and *n*-type SiC epilayers. Work is continuing in order to both fully utilize this growth technique and to further elucidate the growth mechanism of site-competition epitaxy.

The authors gratefully acknowledge J. B. Petit for the resistivity measurements, W. J. Choyke and L. L. Clemen for the low-temperature photoluminescence spectroscopy, E. J. Haugland and J. E. Starr for the Hall measurements, and L. J. Keys and R. L. Allen for performing the CVD experiments.

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